Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Pyridinium aquapyridinebis(salicylato-κ^2O,O')-manganese(III)

Hui-Sheng Wang, Cheng-Bing Ma, Mei Wang, Chang-Neng Chen* and Qiu-Tian Liu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Fuzhou, Fujian 350002, People's Republic of China

Correspondence e-mail: ccn@ms.fjirsm.ac.cn

Received 22 November 2006
Accepted 28 March 2007

Key indicators

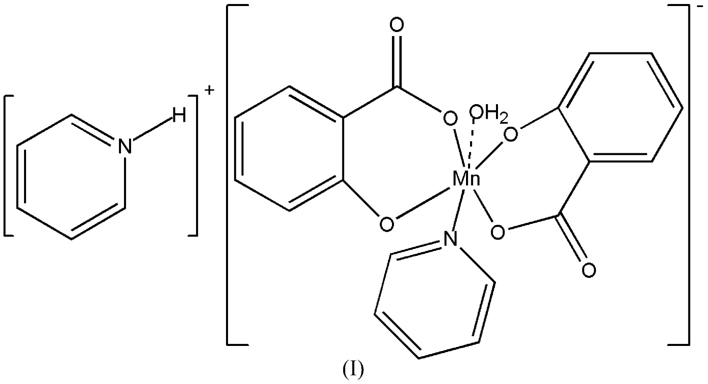
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.122
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_5H_6N)[Mn(C_7H_4O_2)_2(C_5H_5N)(H_2O)]$, is a mononuclear manganese complex in which the Mn atom is six-coordinated by two carboxylate O atoms and two hydroxy O atoms of two salicylates, one O atom of water and one N atom of pyridine.

Comment

Mn^{III} complexes continue to receive attention owing to their pivotal role in such diverse study areas as manganese superoxide dismutase (MnSOD) (Hureau *et al.*, 2005), the oxygen-evolving center (OEC) of photosystem II (Johansson *et al.*, 2003) and numerous single-molecular magnets (Soler *et al.*, 2003). Thus, a complete analysis of the electronic properties of the Mn^{III} ions is necessary in order to understand the role of the metal in these areas. Moreover, salicylic acid, an excellent ligand, is commonly used in metal–organic chemistry, owing to its several possible coordination modes. To date, many mononuclear, dinuclear and multinuclear complexes have been synthesized (Pavacik *et al.*, 1986; Devereux *et al.*, 1995; Christmas *et al.*, 1988).



(I)

Selected bond lengths and angles for (I) are given in Table 1. As shown in Fig. 1, compound (I) is a mononuclear manganese complex and the Mn atom is six-coordinated by two carboxylate O atoms and two hydroxy O atoms of two salicylates, one O atom of water and one N atom of pyridine. Its oxidation state was established to be trivalent by bond-valence sum (BVS) calculations (Liu & Thorp, 1993). The Mn^{3+} ion sits in an axially elongated octahedron due to Jahn–Teller (JT) distortion. The axial sites are occupied by the O atom of H_2O and N atom of pyridine, with the bond lengths [2.239 (2)–2.349 (2) Å] greater than the other Mn—O bond lengths [1.8712 (16)–1.9296 (16) Å].

Intermolecular hydrogen bonds (Table 2) link the molecules together, forming a one-dimensional chain (Fig. 2). These

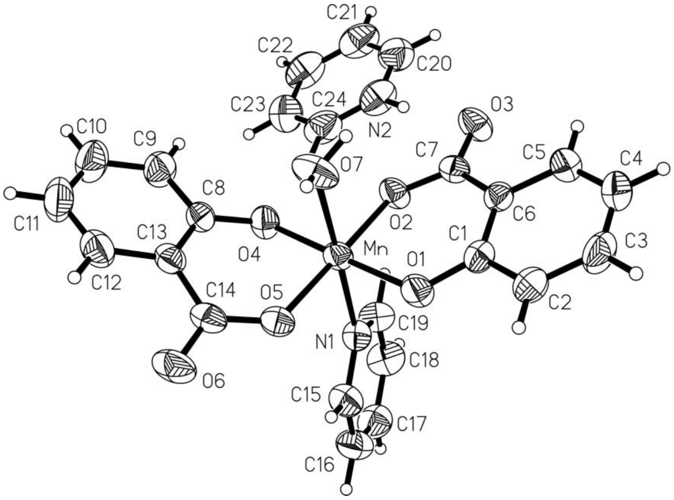


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids.

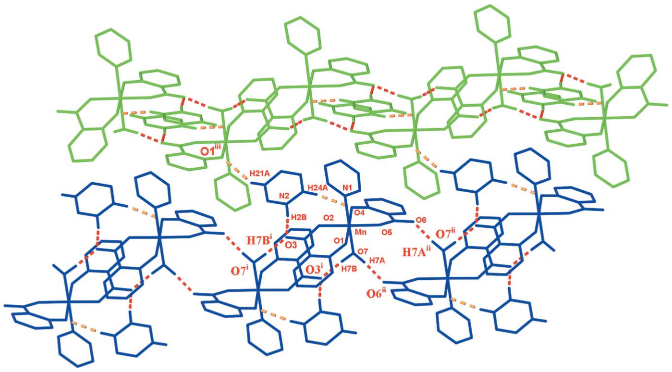


Figure 2
A perspective view of the sheet structure, showing the O—H···O, N—H···O and C—H···O hydrogen-bonding interactions (dashed lines). H atoms other than those involved in hydrogen bonding have been omitted.

chains are further connected through a C21—H21A···O1^{iii} hydrogen bond (Table 2), forming a two-dimensional sheet [symmetry code: (iii) $x + 1/2, -y + \frac{3}{2}, z - \frac{1}{2}$].

Experimental

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. (^{n}Bu$_4$N)[MnO$_4$] was prepared as previously reported (Sala *et al.*, 1978). Mn(OAc)$_2$·4H$_2$O (1.00g, 4.08 mmol) and salicylic acid (4.24g, 30.7 mmol) were dissolved in a mixed solvent comprising pyridine (1.5 ml) and absolute ethanol (20 ml). The resulting solution was stirred while solid (^{n}Bu$_4$N)[MnO$_4$] (0.57g, 1.58 mmol) was added in small portions, giving a black homogeneous solution. This was allowed to stand undisturbed for 10 h, giving a gray precipitate, which was collected by filtration, washed with a mixture of EtOH and Et$_2$O, and dried in air, then dissolved in a mixture of H$_2$O (1.5 ml) and methanol (15 ml). After several days, dark-brown crystals suitable for X-ray crystallography were formed; they were collected by filtration, washed with Et$_2$O, and dried in air.

Crystal data

$(C_5H_6N)[Mn(C_7H_4O_2)_2(C_5H_5N)(H_2O)]$
$M_r = 504.37$
Monoclinic, $P2_1/n$
$a = 12.0499\ (9)$ Å
$b = 11.3964\ (7)$ Å
$c = 16.4446\ (11)$ Å
$\beta = 104.579\ (2)°$
$V = 2185.5\ (3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.65$ mm^{-1}
$T = 295\ (2)$ K
0.3 × 0.2 × 0.1 mm

Data collection

Rigaku MERCURY CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.808$, $T_{max} = 1.000$
16400 measured reflections
5015 independent reflections
3770 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.122$
$S = 1.08$
5015 reflections
319 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mn—O4	1.8705 (16)	Mn—O2	1.9294 (16)
Mn—O1	1.8800 (16)	Mn—O7	2.241 (2)
Mn—O5	1.9194 (16)	Mn—N1	2.349 (2)
O4—Mn—O1	178.62 (7)	O1—Mn—O7	91.97 (8)
O1—Mn—O5	89.93 (7)	O5—Mn—O7	89.68 (7)
O4—Mn—O2	87.49 (7)	O7—Mn—N1	178.10 (7)
O5—Mn—O2	178.85 (7)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7B···O3^{i}	0.90 (3)	1.81 (3)	2.706 (3)	173 (3)
O7—H7A···O6^{ii}	0.90 (3)	1.77 (3)	2.665 (3)	170 (3)
N2—H2B···O3	0.95 (4)	1.84 (4)	2.783 (3)	172 (4)
C24—H24A···O4	0.95	2.46	3.396 (3)	167
C21—H21A···O1^{iii}	0.95	2.60	3.452 (3)	150

Symmetry codes: (i) $-x+2, -y+2, -z+2$; (ii) $-x+1, -y+2, -z+2$; (iii) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

The H atoms bonded to C atoms were positioned geometrically and refined as riding, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, while the H atoms bonded to the N atom and the water molecule were located in a difference Fourier map and refined freely.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

This project was supported by the NNSF of China (No. 20471061) and the Science & Technology Innovation Foundation for the Young Scholar of Fujian Province (No. 2005 J059).

Acta Cryst. (2007). E**63**, m1616–m1618 Wang *et al.* • $(C_5H_6N)[Mn(C_7H_4O_2)_2(C_5H_5N)(H_2O)]$ **m1617**

References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Christmas, C., Vincent, J. T., Chang, H. R., Huffman, J. C., Christou, G. & Hendrickson, D. N. (1988). *J. Am. Chem. Soc.* **110**, 823–830.

Devereux, M., McCann, M., Casey, M. T., Curran, M., Ferguson, G., Cardin, C., Convery, M. & Quillet, V. (1995). *J. Chem. Soc. Dalton Trans.* pp. 771–776.

Hureau, C., Blondin, G., Charlot, M. F., Philouze, C., Nierlich, M., Césario, M. & Mallart, E. A. (2005). *Inorg. Chem.* **44**, 3669–3683.

Johansson, A., Abrahamsson, M., Magnuson, A., Huang, P., Mårtensson, J., Styring, S., Hammarström, L., Sun, L. C. & Åkermark, B. (2003). *Inorg. Chem.* **42**, 7502–7511.

Liu, W. T. & Thorp, H. H. (1993). *Inorg. Chem.* **32**, 4102–4105.

Pavacik, P. S., Huffman, J. C. & Christou, G. (1986). *J. Chem. Soc. Chem. Commun.* pp. 43–44.

Rigaku (2000). *CrystalClear*. Version 1.3.5. Rigaku Corporation, Tokyo, Japan.

Sala, T. & Sargent, M. V. (1978). *J. Chem. Soc. Chem. Commun.* pp. 253–254.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Soler, M., Wernsdorfer, W., Abboud, K. A., Huffman, J. C., Davidson, E. R., Hendrikson, D. N. & Christou, G. (2003). *J. Am. Chem. Soc.* **125**, 3576–3588.

m1618 Wang *et al.* • $(C_5H_6N)[Mn(C_7H_4O_2)_2(C_5H_5N)(H_2O)]$ *Acta Cryst.* (2007). E**63**, m1616–m1618